

**METHOD OF PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION OF
DIAMOND**

This application claims benefit of U.S. Provisional Patent Application No. 60/119,771 filed February 10, 1999, incorporated herein by reference in its entirety.

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FIELD OF THE INVENTION

The present invention relates to a method of synthesizing diamond. In particular, the present invention relates to a method of synthesizing diamond crystals and diamond films using plasma enhanced chemical vapor deposition.

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BACKGROUND OF THE INVENTION

Diamond synthesized by chemical vapor deposition ("CVD") has many unique and outstanding properties that make it an ideal material a broad range of scientific and technological applications. See Y. Tzeng et al., *Application of Diamond Films And Related Materials*, Elsevier Publishers, 1991. A number of methods for diamond
20 CVD are reported which utilize various gas mixtures and energy sources for dissociating the gas mixture. See P.K. Bachmann et al., *Diamond and Related Materials* 1, 1, (1991). Such methods include the use of high temperature electrons in various kinds of plasma, high solid surfaces on hot filaments, and high temperature

gases in combustion flames to dissociate molecules such as hydrogen, oxygen, halogen, hydrocarbon, and other carbon containing gases. Typically, a diamond crystal or film is grown on a substrate, which is usually maintained at a temperature much lower than that of electrons in the plasma, the heated surface of a hot filament, or the combustion flame. As a result, a super equilibrium of atomic hydrogen is developed near the diamond growing surface of the substrate.

Atomic hydrogen is believed to be crucial in the diamond CVD process. It is theorized that atomic hydrogen is effective in stabilizing the diamond growing surface and promoting diamond growth at a CVD temperature and pressure that otherwise thermodynamically favors graphite growth. Consistently, the reported diamond CVD processes involve the use of hydrogen gas or hydrogen containing molecules. The most typical diamond CVD process utilizes a precursor comprising of methane gas diluted by 94-99% hydrogen. With these CVD processes, the super equilibrium of atomic hydrogen can be achieved at a varied percentage of molecular hydrogen in the gas mixture. However, these CVD processes depend on the effectiveness of the dissociation process in generating atomic hydrogen.

Chein et al., Proceedings of the 6th International Conference on New Diamond Science and Technology (1998), report using a high power density microwave plasma to deposit diamond in a precursor comprising of a mixture of methane and hydrogen with less than 50% hydrogen. Growth of diamond from oxy-acetylene flames utilizes a precursor comprising of acetylene and oxygen with a ratio of acetylene to oxygen slightly greater than 1 without additional molecular hydrogen being added. Diamond is deposited in the reducing "inner flame" where atomic hydrogen is a burn product

produced by the high temperature flame. In addition to atomic hydrogen, there are plenty of OH radicals present near the diamond growing surface inside the flame.

OH and O radicals can play another role of atomic hydrogen in the diamond growth process. That is, preferential etching of non-diamond carbon, which results in a net deposition of high purity diamond. Small quantity of oxygen (0.5-2%) or water vapor (<6%) added to the methane and hydrogen precursor is reported to improve diamond crystallinity and lower the diamond CVD temperature. See Saito et al., Journal of Materials Science, 23, 842 (1988), and Kawato et al., J. Applied Physics, 26, 1429 (1987). The quantity, whether small or large, of oxygen and water in a precursor or feedstock is a relative term depending on many other process parameters. Diamond has also been grown in a microwave plasma of a precursor comprising of an acetone/oxygen mixture with a molecular ratio near 1:1. See Chein et al., Proceedings of the 6th International Conference on New Diamond Science and Technology (I 998).

Most of the diamond CVD processes involve the use of one or more compressed gases. Typically, such CVD processes utilize a compressed gas precursor comprising of 1 vol.% methane gas diluted by 99 vol.% hydrogen. These gases usually must be precisely controlled by electronic mass flow controllers to ensure the accurate composition in the gas precursor feed.

In U.S. Patent No. 5,480,686 to Rudder et al. ("*Rudder*") a method of diamond growth is disclosed that utilizes a radio frequency ("RF") plasma in a precursor comprising of a mixture of water (more than 40%) and alcohol. No compressed gases are needed for this diamond CVD process. However, water has a low vapor pressure

at room temperature, and condensation of water in the cooler part of the reactor manifold may be a concern. Also, water has a high freezing temperature making it easy to freeze at the orifice of a flow controller where liquid vaporizes and enters a low pressure reactor chamber. Buck et al. ("*Buck*"), "Microwave CVD of diamond using methanol-rare gas mixtures," Materials Research Society Symposium Proceedings, Vol. 162, 97-102, 1989.) have grown clusters of diamond crystallites on small (2-4 mm²) silicon substrates that were scratched with a diamond tip or mechanically polished with 3 μm diamond powder by microwave plasma enhanced CVD in pure methanol vapor. Argon gas additive was found necessary for high quality diamond to be deposited in the methanol vapor. When it is fully dissociated and reacted in the plasma, the pure methanol vapor plasma contains a C/O/H composition similar to that of CO/H₂ plasma, which has been used for successful deposition of diamond by means of electrical discharges. See Ito et al., Proceedings of International Conference on New Diamond Science and Technology, p.2-16 (1988).

In a typical electrical discharge such as a microwave plasma, electrons with an average temperature exceeding 10,000°C are abundant. These energetic electrons effectively dissociate molecular species and generate a high concentration of radicals necessary for the deposition of diamond and the preferential etching of non-diamond deposits without needing a high temperature filament. Hot filament assisted CVD processes employ solid surfaces at a temperature of about 2,000° C-2,500° C to dissociate molecules and generate radicals necessary for diamond deposition. The hot filament temperature is much lower than that of energetic electrons in a plasma. As a

consequence, hot-filament CVD of diamond in CO/H₂ mixtures has not been successful even though the same gas mixtures have been routinely used for plasma assisted deposition of diamond films.

- Nevertheless, the plasma enhanced CVD method is desirable because diamond
- 5 crystals and films can be deposited on large-area and/or irregularly shaped objects using inexpensive equipment. Thus, there remains a need for an economic method of synthesizing diamond utilizing plasma enhanced CVD. Further, there remains a need for a method of diamond CVD which preferentially etch non-diamond deposits at low substrate temperatures to provide the deposition of high quality diamond.
- 10 Additionally, there remains a need for a method of diamond CVD that does not require the use of compressed gases or water or precision electronic mass flow controllers. It is to the provision of a method of plasma enhanced CVD of diamond that meets these needs that the present invention is primarily directed.

SUMMARY OF THE INVENTION

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Briefly described, the present invention relates to a method of synthesizing diamond that enables the economic growth of high quality diamond crystals and diamond films using a liquid solution as the feedstock and an electrical discharge as the means of dissociating and reacting the vapor of the said solution. In the method of the present invention, a precursor comprising at least one carbon containing compound having a carbon to oxygen ratio greater than one is fed into a deposition chamber through a liquid flow controller such as a needle valve. The precursor further comprises a solution of methanol and at least one carbon containing compounds having a carbon to oxygen ratio greater than one. The solution is pre-mixed prior to entering the deposition chamber. Such carbon containing compounds include ethanol, isopropanol, and acetone. The solution vaporizes as it enters the low pressure deposition chamber. The vaporized precursor comprises the same composition as the solution. When the vapor passes through an electrical discharge zone, it is dissociated to generate OH, H, O, CH₃ and other molecules and radicals.

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Ans

A 7 ~~The substrate generally is sheet or wafer of silicon, copper, aluminum and molybdenum. Some of the substrates are polished using 1 μ m diamond paste prior to the deposition process. Typically, the substrate is mounted on a water cooled substrate holder. The substrate can be either in touch with the plasma or at a distance from the plasma. In experiments using the method of the present invention, the substrate was in touch with a microwave plasma ball generated inside a cylindrical microwave cavity. The reactor chamber pressure generally is maintained between 1~~

plasma in the vapor of a precursor solution comprising 3.5 grams of acetone and 100 grams of methanol.

Figure 7 is a graphic illustration of a Raman spectrum for the diamond film of Figure 6.

5 Figure 8 is an optical micrograph of a diamond film deposited in accordance with the present invention on an aluminum plate by a microwave plasma in the vapor of a precursor solution comprising 15 grams of acetone and 100 grams of methanol.

Figure 9 is a graphic illustration of a Raman spectrum for the diamond film of Figure 8.

10 Figure 10 is an optical micrograph of diamond crystallites grown in accordance with the present invention on a clean and untreated silicon wafer by a microwave plasma in the vapor of a precursor solution comprising 50 grams of acetone and 100 grams of methanol.

Figure 11 is a graphic illustration of a Raman spectrum for a diamond
15 crystallite of Figure 10.

Figure 12 is an optical micrograph of a diamond film deposited in accordance with the present invention on a clean and scratched (by diamond paste with 1 μm diamond powder) silicon wafer by a microwave plasma in the vapor of a precursor solution comprising 50 grams of acetone and 100 grams of methanol.

20 Figure 13 is a graphic illustration of a Raman spectrum for the diamond film of Figure 12.

Figure 14 is an optical micrograph of diamond crystallites grown in accordance with the present invention on a clean and untreated silicon wafer by a

microwave plasma in the vapor of a solution comprising 100 grams of isopropanol and 100 grams of methanol.

Figure 15 is a graphic illustration of a Raman spectrum for the diamond crystallites of Figure 14.

5 Figure 16 is an optical micrograph of diamond crystallites deposited in accordance with the present invention on a clean and untreated silicon wafer by a microwave plasma in the vapor of a precursor comprising isopropanol.

Figure 17 is a graphic illustration of a Raman spectrum for the diamond crystallites of Figure 16.

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DETAILED DESCRIPTION OF THE INVENTION

For a more complete understanding of the present invention, reference should be made to the following detailed description taken in connection with the accompanying figures.

The present invention relates to a method of synthesizing diamond crystals and
15 diamond films for a very broad range of scientific and technological applications such as optical windows, machining tools, heat spreaders, tribological coatings, sensors and actuators, electrochemical coatings, protective coatings, and wide-bandgap semiconductor devices. The method of the present invention uses a premixed methanol-based liquid solution as the feedstock. The methanol-based solution
20 contains 0.5-99.5% by weight of one or more carbon containing compounds with the molar ratio of atomic carbon to atomic oxygen being greater than one. Although water and other compounds that can be dissociated by a plasma to form O, H, F, Cl, Br, and OH radicals may be added to the methanol-based solution, it is not a

requirement for the deposition of diamond crystals and diamond films by the method of the present invention.

7 Figure 1 generally illustrates the plasma enhanced chemical vapor deposition system utilized in performing the method of the present invention. As illustrated in Fig. 1, the precursor 5 is fed from a precursor container 4 by a conduit 6, such as a TEFLON or metal tubing, through a liquid flow controller 7, such as a needle valve, to an inlet 2 of reactor chamber 1. The reactor chamber 1 is formed from a material capable of withstanding the temperature generated during the CVD process. In the present invention, the reactor chamber 1 is stainless steel and typically 8" in diameter. When the liquid precursor 5 enters the low pressure side of the liquid flow controller 7, it vaporizes to form a vapor precursor 5 comprising a mixture with the same molar composition as the liquid precursor 5. In addition to inlet 2, the reactor chamber 1 has an outlet 3 connected to a mechanical vacuum pump 13 through an automatically controlled throttle valve 14 to maintain constant pressure in the reaction chamber 1 throughout the deposition process and for circulating the vapor of the precursor 5 through the reactor chamber 1. The vapor precursor 5 is maintained at a pressure within the vacuum chamber 1 of between 1 mtorr and 250 torr, with the pressure being monitored by a pressure gauge (not shown).

Electromagnetic energy 8 discharged at various frequencies, for example, DC, RF, and microwave, and also high frequency electromagnetic energy such as energy discharged from a laser, is applied to the reactor chamber 1. A window 9 such as a quartz window that separates the low pressure reactor from ambient pressure and permit microwave energy to progate into the reaction chamber 1. Preferably, the

electromagnetic energy 8 is microwave energy. The reactor chamber 1 is a part of the cylindrical cavity for the microwave of 2.45 GHz. A substrate 11 is placed on a substrate holder 12, preferably a water cooled substrate holder to control the temperature of and cool the substrate 11. Substrate 11 temperature is monitored with
5 a dual color optical pyrometer (not shown). The plasma 10 dissociates the vapor precursor 5 and releases OH, H, O, CH₃, CH₂, etc. radicals for a net deposition of diamond on a substrate surface 15. Methanol vapor (CH₃OH) has a carbon to oxygen ratio equal to one. In the present invention, when methanol dissociates, it forms high concentrations of radicals that rapidly etch carbon, including diamond, resulting in
10 slow growth of diamond in areas where a diamond deposition rate exceeds the etching rate. The growth rate and degree of non-uniformity also depend on the exposure of carbon, which may be present in some reactor fixtures or previously coated on reactor walls or the substrate holder, to the methanol plasma.

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15 ~~When the precursor 5 comprises a solution of methanol and a proper quantity~~
of one or more carbon containing compounds having a carbon to oxygen ratio greater than one, diamond growth is substantially uniform, reproducible, and at a higher growth rate than conventional CVD methods. For example, ethanol (CH₃CH₂OH), isopropanol, ((CH₃)₂CHOH), and acetone (CH₃COCH₃) have respective carbon to oxygen ratios of 2, 3, and 4. The selection of the carbon containing compound is not
20 limited to ethanol, isopropanol, or acetone, and may be selected from other such carbon containing compounds having carbon to oxygen ratios greater than one. In addition, as indicated in Example 8 below, under certain CVD conditions, it is not required for the precursor 5 to contain methanol. However, if the precursor comprises

range from sub-micrometers to more than 500 μm .

An electromagnetic, such as microwave, plasma enhanced chemical vapor deposition technique using a precursor comprising methanol-based solutions or a carbon containing compound having a carbon to oxygen ratio greater than one as the feedstock has been developed for the deposition of diamond crystals and diamond films. The OH, H, O radicals generated by the dissociation of the precursor vapor are shown to be sufficient in suppressing the growth of graphitic and amorphous carbon, which results in the net deposition of diamond by the carbon containing radicals that were dissociated from the same vapor. By the addition of carbon containing compounds having a carbon to oxygen ratio greater than one to methanol, the diamond growth rate increases by orders of magnitude over conventional methods.

The aforementioned precursors are less costly than the typical compressed gases that are often used for diamond deposition. Further, the mixing of a methanol-based solution can be performed under standard conditions without the need for an expensive precision electronic mass flow controller.

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~~In contrast to what was reported by Buck, who deposited clusters of diamond crystallites in a small area of 3-4 mm² in a methanol plasma, when methanol was used alone as the precursor feedstock for substrates of 25 mm x 25 mm in size or larger, only the area near the edge showed acceptable diamond nucleation density in some cases. The diamond deposition was highly non-uniform across the substrate surface. In other cases, too much oxidizing and carbon etching radicals were generated in the methanol plasma resulting in a very slow growth of diamond. For example, when 2,000 W microwave was applied at a pressure of 80 torr and a substrate temperature~~

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of 900° C, the methanol plasma deposited only about 2 μm diamond on a molybdenum substrate after 40 hours of deposition. The diamond growth rate is only 0.05 μm per hour in this case. Using a solution comprising of methanol and one or more carbon containing compounds, that have carbon to oxygen ratio being greater than one, diamond deposition rates of more than two orders of magnitude have been achieved in the present invention.

EXAMPLES

A. Substrate pre-treatment and cleaning.

Substrates of silicon, aluminum, and molybdenum were cleaned by acetone and methanol before being loaded onto the substrate holder. Except those substrates specified to be untreated, all substrates were polished with diamond paste containing 1 μm sized diamond particles.

B. Deposition parameters.

a47 Typical deposition parameters are as follows:

Microwave power	600-3000W
Vapor pressure	1 mtorr-250 torr
Substrate temperature	300° C-1600° C
Methanol	0.5-99.5% by weight
Ethanol, isopropanol, and acetone	0.5-99.5% by weight

C. Diamond film characterization methods.

A Normaski phase contrast optical microscope was used to examine the crystal shapes and surface morphology of the deposited films. Diamond grains with

100 or 111 facets can clearly be seen using this optical microscope. The diamond film thickness can also be measured by examining the cross-sectional view of such films using the same optical microscope. A micro Raman spectrometer powered by an Argon ion laser was used to examine the phase purity of the deposited films.

- 5 Diamond peak around 1332 cm^{-1} provided convincing evidence that the deposited carbon films were diamond.

The following examples are provided to illustrate the present invention but are not to be construed as limiting the invention in any way.

Example 1

- 10 A liquid solution comprising 4.6 grams of ethanol and 100 grams of methanol was used as the precursor feedstock. A molybdenum plate of 1/2 inch thick and 2 inches in diameter was polished by diamond paste containing $1\text{ }\mu\text{m}$ sized diamond powder and cleaned by acetone and methanol. Microwave power of 2kW was applied at the vapor pressure of 80 torr resulting in the substrate being heated to $1,000^{\circ}\text{C}$.
- 15 After 45 hours of deposition, the film separated itself from the molybdenum substrate and was of about $45\text{ }\mu\text{m}$ in thickness. The growth rate was about $1\text{ }\mu\text{m}$ per hour. Diamond growth rate increased with increasing quantity of ethanol in the methanol-based solution. Figure 2 shows the optical micrograph of the ~~free~~^{Free}-standing diamond film. The diamond peak at 1332 cm^{-1} in the Raman spectrum shown in Figure 3
- 20 indicates that the diamond film is of very good quality.

Example 2

A liquid solution comprising 4 grams of isopropanol and 100 grams of methanol was used as the precursor feedstock. A molybdenum plate of 1/2 inch thick

and 2 inches in diameter was polished by diamond paste containing 1 μm sized diamond powder and cleaned by acetone and methanol. Microwave power of 2kW was applied at the vapor pressure of 80 torr resulting in the substrate being heated to 1,000° C. After 22 hours of deposition, the film separated itself from the molybdenum substrate and was of about 44 μm in thickness. The growth rate was about 2 μm per hour. Figure 4 shows the optical micrograph of the free-standing diamond film. The clear diamond peak in the Raman spectrum shown in Figure 5 indicates that the diamond film is of good quality.

Example 3

10 A liquid solution comprising 3.5 grams of acetone and 100 grams of methanol was used as the precursor feedstock. A silicon wafer of 1" x 1" in size was placed on a water cooled molybdenum holder. The silicon wafer was polished by diamond paste containing 1 μm sized diamond powder and cleaned by acetone and methanol before loading onto the substrate holder. Microwave power of 2kW was applied at the vapor pressure of 60 torr resulting in the substrate being heated to 1030° C. After 23 hours of deposition, the diamond film was about 30 μm in thickness. The growth rate was about 1.3 μm per hour. Figure 6 shows the optical micrograph of the diamond film on silicon. The diamond peak at 1332 cm^{-1} in the Raman spectrum shown in Figure 7 indicates that the diamond film is of good quality.

Example 4

20 A liquid solution comprising 15 grams of acetone and 100 grams of methanol was used as the precursor feedstock. An aluminum plate of 2" diameter was placed on a water-cooled molybdenum holder. The aluminum plate was polished by diamond

paste containing 1 μm sized diamond powder and cleaned by acetone and methanol before loading onto the substrate holder. Microwave power of 650 W was applied at a vapor pressure of 11 torr, resulting in the substrate being heated to 535° C. After 5 hours of deposition, the microwave power was increased to 800 W, and the vapor pressure was increased to 16 torr for another 5 hours of deposition at 613° C. A continuous diamond film was coated onto the aluminum plate with good adhesion. Figure 8 shows the optical micrograph of the diamond film on aluminum. The diamond peak at 1332 cm^{-1} in the Raman spectrum shown in Figure 9 indicates that the coating was indeed a diamond film.

10 **Example 5**

A liquid solution comprising 50 grams of acetone and 100 grams of methanol was used as the precursor feedstock. A silicon wafer of 1" x 1" in size was placed on a water-cooled molybdenum holder. The silicon wafer was cleaned by acetone and methanol but not polished by diamond paste before loading onto the substrate holder. Microwave power of 1,100 W was applied at a vapor pressure of 35 torr, resulting in the substrate being heated to 724°C. After 2 hours, diamond nucleated and grew to the size of about 4 μm . The growth rate was about 2 μm per hour. Figure 10 shows the optical micrograph of the diamond crystallites on the untreated silicon wafer. The diamond peak at 1332 cm^{-1} in the Raman spectrum shown in Figure 11 indicates that the diamond crystallites are of good quality.

Example 6

A liquid solution comprising 50 grams of acetone and 100 grams of methanol was used as the precursor feedstock. A silicon wafer of 1" x 1" in size was placed on a



water-cooled molybdenum holder. The silicon wafer was polished by diamond paste containing 1 μm sized diamond powder and cleaned by acetone and methanol before loading onto the substrate holder. Microwave power of 1,100 W was applied at a vapor pressure of 29 torr, resulting in the substrate being heated to 800° C. After 4 hours of deposition, a diamond film was deposited. Figure 12 shows the optical micrograph of the diamond film on silicon. The diamond peak at 1332 cm^{-1} in the Raman spectrum shown in Figure 13 indicates that the diamond film is of good quality. In addition to the diamond peak, the Raman spectrum shows another broad band around 1550 cm^{-1} indicating the inclusion of non-diamond phases in the diamond grains, in the grain boundaries, or in both.

Example 7

A liquid solution comprising 100 grams of isopropanol and 100 grams of methanol was used as the precursor feedstock. A silicon wafer of 1" x 1" in size was placed on a water-cooled molybdenum holder. The silicon wafer was cleaned by acetone and methanol, but not polished by diamond paste, before loading onto the substrate holder. Microwave power of 1kW was applied at a vapor pressure of 36 torr, resulting in the substrate being heated to 754° C. After 2 hours and 40 minutes, diamond nucleated and grew to the size of about 7 μm . The growth rate was about 2.7 μm per hour. Figure 14 shows the optical micrograph of the diamond crystallites on the untreated silicon wafer. The diamond peak at 1332 cm^{-1} in the Raman spectrum shown in Figure 15 indicates that the diamond crystallites are of good quality.

Example 8

Substantially pure isopropanol was used as the precursor feedstock. A silicon

wafer of 1" x 1" in size was placed on a water-cooled molybdenum holder. The silicon wafer was cleaned by acetone and methanol, but not polished by diamond paste, before loading onto the substrate holder. Microwave power of 900 W was applied at a vapor pressure of 30 torr, resulting in the substrate being heated to 740° C. After 2 hours and 14 minutes, diamond nucleated and grew to the size of about 2 μm . The growth rate was about 1 μm per hour. Figure 16 shows the optical micrograph of the diamond crystallites on the untreated silicon wafer. The diamond peak at 1332 cm^{-1} in the Raman spectrum shown in Figure 17 indicates that the crystallites are indeed diamond. The much stronger background signal and the higher broad band near 1550 cm^{-1} in the Raman spectrum shown in Figure 17 as compared to those shown in Figure 15 indicate that the quality of the diamond crystallites was improved by the addition of methanol to isopropanol.

Although the invention has been described in detail for the purpose of illustration, it is understood that such detail is solely for that purpose, and variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention which is defined by the following claims.